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Letter

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Electrolyte-induced Instability of Colloidal Dispersions in Nonpolar Solvents

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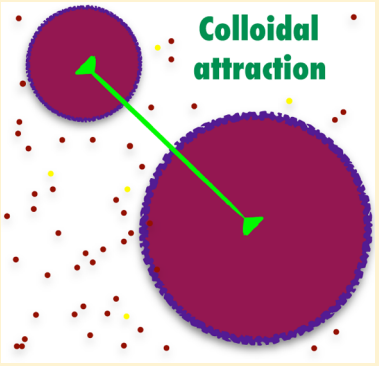
Supporting Information

ABSTRACT: Dispersions of poly(methyl methacrylate) (PMMA) latexes were prepared in a low dielectric, nonpolar solvent (dodecane) both with and without the oil-soluble electrolyte, tetradodecylammonium-tetrakis(3,5-bis(trifluoromethyl)phenyl)borate. For dispersions with a high concentration of background electrolyte, the latexes become colloidally unstable and sediment in a short period of time (<1 h). This is completely reversible upon dilution. Instability of the dispersions is due to an apparent attraction between the colloids, directly observed using optical tweezers by bringing optically trapped particles into close proximity. Simple explanations generally used by colloid scientists to explain loss of stability (charge screening or stabilizer collapse) are insufficient to explain this observation. This unexpected interaction seems, therefore, to be a consequence of the materials that can be dispersed in low dielectric media and is expected to have ramifications for studying colloids in such solvents.



The Derjaguin−Landau−Verwey−Overbeek (DLVO) theory is one of the classic foundations in the field of colloid science; it describes the stability of colloids as a balance of attraction (van der Waals dispersion forces) and repulsion (electrostatic forces).[1,2] Later, other ways to control colloidal interactions were developed, such as steric repulsion, for example, where nonionic macromolecules anchored to the surface overlap.[3]

Generating new ways to mediate colloidal stability and instability would be highly beneficial for controlling the properties of nanoparticles, particularly in nonpolar solvents, where charge numbers are typically low and van der Waals attractions are weak. In this Letter, a classic system in colloid science is used: poly(methyl methacrylate) (PMMA) latexes coated with poly(12-hydroxystearic acid) (PHSA) brushes in dodecane solvent.[4] This system is an extremely popular tool for experimental studies of hard spheres.[5−12] The particles are always considered in the literature to be sterically stabilized. That the particles are sterically stabilized, however, does not necessarily mean that they are uncharged.[13−16] In this Letter, the effect of adding an oil-soluble electrolyte on the colloidal interactions is studied. If there were no interactions other than attraction (dispersion) and repulsion (steric and electrostatic), then the addition of salt would have no influence on stability. The electrolyte would reduce the screening length of the electrostatic interaction, but the polymer brushes would still act as steric stabilizers. As the results show, an effective attraction can be induced between the colloids in high concentrations of electrolyte. That the addition of an electrolyte destabilizes a colloidal dispersion is an unexpected observation that cannot be explained using existing simple theories of colloidal stability.

Dispersions of PMMA latexes (AC12, containing $DiIC_{18}$ dye, a = 775 ± 25 nm) were prepared in dodecane at a volume fraction (ϕ) of 3.7 × 10^{-4}. The oil-soluble compound tetradodecylammonium-tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate ($NDod_4$-TFPhB), known to be soluble in nonpolar solvents,[17] was used as the electrolyte. (Details of the synthesis are given in the Supporting Information.) Despite being soluble, electrolytes in nonpolar solvents tend to have much lower saturation concentrations than salts in water.[18,19]

Given the extensive literature on these latexes being sterically stabilized, the assumption would be that they would be stable when electrolyte is added. However, this is not the case. When viewing the latexes in an optical microscope (Figure 1b), large clusters of latexes are observed. This is only the case in the highest concentration solution of electrolyte studied (0.34 mM). The latexes in the absence of electrolyte (Figure 1a) are isolated, as would be expected for sterically stabilized colloids.

These clusters form through an apparent attraction between the colloids. This was observed directly by optically trapping clusters of colloids and then bringing them into close proximity. Two single colloids could be brought together in a single trap and aggregated into a pair, although holding them in the trap for a small amount of time is required before this happens. This is consistent with repulsion and attraction that are separation-dependent. As the number of colloids in a cluster increases, however, the attraction occurs instantaneously. This is perhaps unsurprising given some observations in the literature. It is known that geometric confinement can result in colloidal

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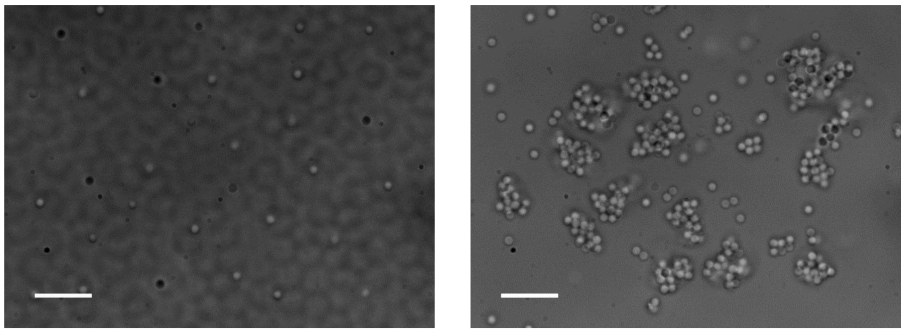
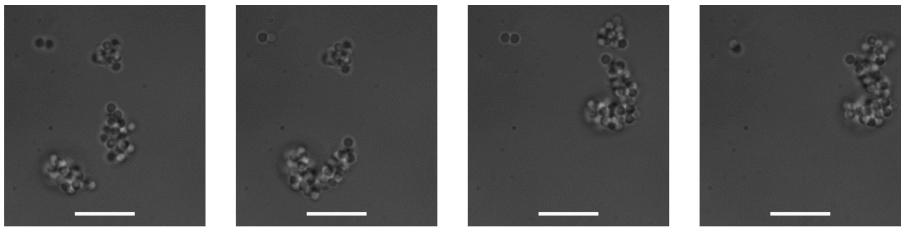


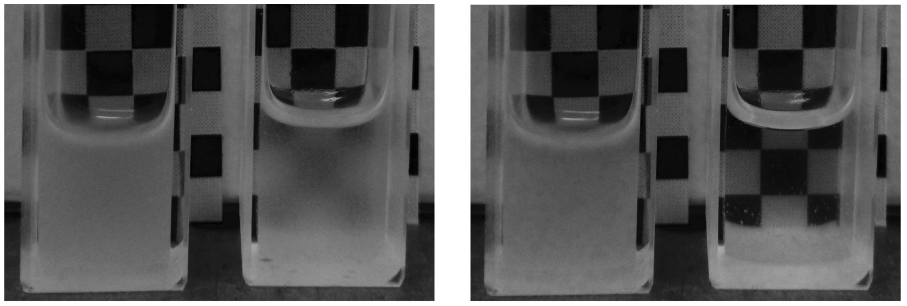
(a) Without electrolyte (b) 0.34 mM electrolyte

Figure 1. Images of clusters of latexes in either electrolyte-free dodecane (a) or a solution of 0.34 mM electrolyte (b). In dodecane alone, the latexes are stable. In a 0.34 mM solution of electrolyte, however, large clusters of many colloids are formed. The scalebars represent 10 μm.



(a) (b) (c) (d)

Figure 2. Two clusters of latexes in dodecane with a high concentration of electrolyte (0.34 mM) are optically trapped (a) and brought together (b). They immediately attract at contact (c) to form a larger aggregate. One trap is then used to maneuver the newly formed aggregate, which also remains stable in the absence of any optical trap (d). These are stills from a video in the Supporting Information. The scalebars represent 10 μm.



(a) $t = 0$ (b) $t = 1$ h

Figure 3. Stability of dispersions of latexes ($\phi = 3.7 \times 10^{-4}$) in dodecane both without (left) and with (right) added $NDod_4$-TFPhB electrolyte (0.34 mM). Images were taken of the dispersions as initially prepared (a) and after 1 h sedimentation (b). Without electrolyte, only a small amount of sedimentation is observed due to the size of the latexes and the density mismatch; with electrolyte, the dispersion completely sediments.

attraction[20] and that the strength of many-body repulsion is less than pairwise repulsion.[21] The process of aggregation is shown in Figure 2 and in a video in the Supporting Information. As the colloids form a cluster, they are randomly distributed, which shows that the attraction is nondirectional, as seen in Figure 1. This stands in contrast with highly directional dipole chaining,[22] for example. The increase in attraction as the cluster aggregation number increases suggests that they form through a chain-reaction mechanism. The formation of colloidal pairs may not be favored, but once pairs form, the aggregation into higher number clusters proceeds rapidly.

The colloidal attraction that results in the formation of clusters (Figures 1 and 2) has macroscopic as well as microscopic consequences. The colloidal stability of dispersions with different concentrations of $NDod_4$-TFPhB electrolyte is dramatically different. Optical images of the dispersions with varying concentrations of electrolyte were taken as a function of time, and the results from the electrolyte-free dispersion and the high-electrolyte concentration dispersion are shown in Figure 3. (A low-electrolyte concentration dispersion was equivalently stable to the electrolyte-free dispersion.) It is clear that the addition of a high concentration of electrolyte destabilizes the dispersions, but a large concentration is required to achieve instability. Sedimentation of colloids in electrolyte solutions must be due to particle aggregation, which increases the size of the sedimenting object.

This attraction is completely reversible and is due to the presence of the electrolyte. A sample of aggregated, undyed latexes in dodecane was split into two. One of these samples was then centrifuged before the supernatant was removed and repeatedly replaced with fresh dodecane. The sample was finally made up in dodecane to match the original volume fraction and redispersed. This sample was found to be completely stable again. (Images are shown in the Supporting Information.)

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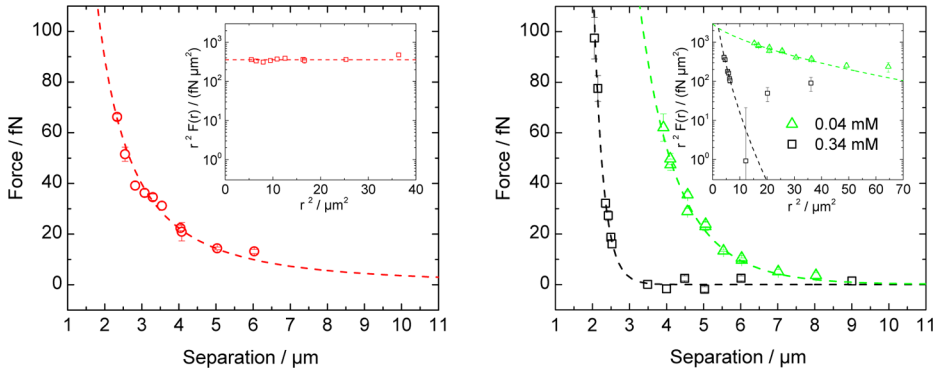

(a) Without electrolyte (b) With electrolyte

Figure 4. Interaction forces between latexes, either without electrolyte (a) or with electrolyte (b), measured via the blinking optical tweezers technique. The data are fit to eq 1 (dashed lines), confirming that the latexes are charged regardless of the electrolyte concentration.

It is important to stress that this instability is also observed for other types of related systems and therefore does not depend on the specific constituents of the colloid. Data for one set of latexes in one solvent is exclusively discussed in this Letter, but this observation of colloidal instability due to added electrolyte has been made for several systems of PMMA latexes in nonpolar solvents. Dyed, undyed, and ionic monomer containing latexes in both dodecane and cyclohexane are all destabilized in high concentration solutions of electrolyte. (Data relating to the other systems are shown in Supporting Information.) This therefore appears to be a feature of dispersions of these polymer colloids in electrolyte solutions in nonpolar solvents, not a specific result due to one particular solvent or latex functionality.

This raises the question of the origin of this apparent attraction. Two possibilities, commonly used to explain colloidal stability, will be discussed in turn: negating charge repulsion due to electrolyte screening and collapse of the steric stabilizer layer.

Interparticle pairwise interactions were measured using blinking optical tweezers.[23,24] The interparticle force ($F(r)$) is determined as a function of the initial particle separation r. Details of the optical system are given in the Supporting Information. $F(r)$ is then plotted as a function of the separation and fit to eq 1 to extract the particle charge ($Z = Ne$, where N is the number of charges and e is the elementary charge) and the screening length (κ^{-1}), where ϵ_0 is the vacuum permittivity, ϵ_r is the relative permittivity, and a is the particle radius.

$$F(r) = \frac{Z^2}{4\pi\epsilon_0\epsilon_r}\frac{\exp(-\kappa(r-2a))}{(1+\kappa a)^2}\left(\frac{1}{r^2}+\frac{\kappa}{r}\right) \quad (1)$$

The forces measured for latexes in systems with three concentrations of electrolyte measured using blinking optical tweezers are shown in Figure 4. The repulsion is found to be as expected for the concentration of electrolyte. For the electrolyte-free dispersion, there is a nonzero and long-ranged repulsive force, as expected for charged colloids. The interaction is long-range due to the lack of background electrolyte; the latexes interact with a purely Coulombic repulsion (see Figure 4a, inset). Because of the magnitude of the interparticle interaction, it is not possible to measure forces at shorter separations, meaning that it is not possible to directly observe attraction using this apparatus. The force−separation curve fit to an unscreened Coulomb function gives a charge per particle of $Z = 56 \pm 1$ e. (Similar values are found for undyed latexes, and a force−separation curve is shown in the Supporting Information.) In the 0.04 mM electrolyte solution, a screened-Coulombic repulsion is observed (with a charge of $Z = 147 \pm 1$ e), and the interaction is over a finite length scale as expected given that electrolyte has been added ($\kappa^{-1} = 1.62 \pm 0.1$ μm). In the 0.34 mM electrolyte solution, a repulsion can also be measured ($Z = 183 \pm 2$ e). The interaction is over a shorter length scale ($\kappa^{-1} = 0.30 \pm 0.02$ μm). The screening length in this system can be predicted from conductivity measurements (shown in the Supporting Information), and the fitted values of κ^{-1} agree well with those predicted from the conductivity. From these blinking optical tweezer results, it is clear that the latexes are still experiencing a repulsive force over long length scales; therefore, the force of attraction must be strong and short-ranged.

Screening of particle charges therefore is insufficient to explain the colloidal instability. The repulsive Coulombic force is still strong at moderate interparticle separations. Additionally, if only the repulsion was removed, then the colloids would interact as hard spheres, which are not attractive. For the steric layer to be ineffective, the addition of the electrolyte would have to cause a modification of the structure of the brush copolymer. The impact that the electrolyte has on polymer micelles of the PHSA polymer was studied by small-angle neutron scattering (SANS), using an approach previously developed to characterize the interaction of surfactants and the stabilizer.[25] (SANS data is shown in the Supporting Information.) The scattering from the PHSA polymer micelles in electrolyte-free dodecane and a solution of electrolyte in dodecane are found to be identical. Therefore, the addition of electrolyte causes no change to the PHSA stabilizer polymer, and this cannot be responsible for the colloidal attraction.

The observations discussed in this Letter show that an apparent attractive force is induced between colloids in solutions of an electrolyte in nonpolar solvents at high concentrations. No such instability has ever been reported for these model PMMA colloids in nonpolar solvents, which, when dispersed with electrolyte, have generally been in solutions of surfactants or small molecule electrolytes or the electrolyte used in this study at low concentrations.[15,26−30] The attraction cannot be explained by existing simple theories. When salt is present, there is still charge sphere repulsion at moderate separations, and the PHSA stabilizer is unperturbed. An explanation of this observation will, therefore, require the apparent attraction to come from another source. Both the

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nature of the chemical species present and the way they impact interparticle interactions will need to be considered. Regardless of the origin, this observation does offer a new way of controlling the interactions between colloids in nonpolar solvents. Future experimental and theoretical work to determine the exact nature of this observation are warranted to fully characterize the influence that electrolytes have on colloidal stability in low dielectric media, specifically, and to see if it is possible to design systems to generalize this to other solvents.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.7b01685.

Synthetic method and analytical chemistry of $NDod_4$-TFPhB electrolyte, details of redispersion experiment, results showing instability for other PMMA latexes, measurement of charge of undyed PMMA latexes, electrical conductivity measurements of electrolyte solutions, and small-angle neutron scattering results. (PDF)

Videos of particle attraction. (AVI)

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Notes

The authors declare no competing financial interest.
Data are also available from the Zenodo repository at DOI: 10.5281/zenodo.884821.

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